

Studies of intersystem crossing dynamics in acetylene

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(Received 7 February 2007; accepted 23 March 2007; published online 14 May 2007)

We report a new *ab initio* study of the acetylene T_3 potential energy surface, which clarifies the nature of its energy minimum, and present computed equilibrium geometries and diabatic frequencies. This information enables the computation of harmonic vibrational overlap integrals of T_3 vibrational levels with the S_1 $3\nu_3$ state. The results of this calculation support the interpretation of two local perturbations of S_1 $3\nu_3$, revealed in ultraviolet laser-induced fluorescence/surface electron ejection by laser excited metastables spectroscopy and Zeeman anticrossing measurements, respectively, as arising from two rotational submanifolds of a single T_3 vibrational state. We present plausible assignments for this state as a guide for future experimental work. © 2007 American Institute of Physics. [DOI: 10.1063/1.2730832]

I. INTRODUCTION

The mechanism of intersystem crossing in the acetylene molecule has attracted considerable experimental and theoretical attention for many years. Attention has focused on a particular vibrational mode of the S_1 $\tilde{A}^1 A_u$ electronic state, the ν_3 symmetric CCH bending vibration, as a promoter of coupling to the triplet manifold. Several lines of experimental evidence reveal a monotonic increase in coupling to triplet levels with increasing quanta of ν_3 . One measure of such coupling is the density of Zeeman anticrossings (ZAC) (described further below), which was found to increase steadily with ν_3 until, in $4\nu_3$, the anticrossings became too densely spaced to resolve.¹ This increase in coupling to triplets is much more rapid than the increase in density of triplet vibrational states. Thus it is a matrix element rather than a density of states effect. But why should the $S_1 \sim T$ matrix element increase rapidly with excitation in S_1 ν_3 ? This is a vibrational overlap effect associated with the near-linear turning point of vibrational levels on the S_1 and T_3 potential surfaces.

In 1987, Ochi and Tsuchiya^{2,3} recorded the laser-induced fluorescence (LIF) spectra of the $\tilde{A}^1 A_u \leftarrow \tilde{X}^1 \Sigma_g^+ V_0^2 K_0^1$, $V_0^3 K_0^1$, and $V_0^4 K_0^1$ subbands in a molecular beam at moderate (0.1 cm^{-1}) resolution. (Here V denotes the *trans*-bend mode, ν_4'' in the $\tilde{X}^1 \Sigma_g^+$ ground electronic state and ν_3' in the $\tilde{A}^1 A_u$ excited state, and K denotes the projection of total angular momentum J along the a axis, ℓ'' in the \tilde{X} state, and K_a' in the \tilde{A} state. The subscript is the lower state quantum number, and the superscript is the upper state quantum number; i.e., V_n^m refers to a transition that connects the $m\nu_3'$ and $n\nu_4''$ vibrational levels.) In the spectra of Ochi and Tsuchiya, an especially large degree of fractionation was observed in the rotational lines of $V_0^3 K_0^1$. Quantum beats were also seen in the fluorescence decay of some of these levels, the frequency and intensity of which were modified in the presence of mag-

netic fields. These authors proposed both that the $\tilde{A}^1 A_u$ $3\nu_3$ level is strongly mixed with a bath of triplet vibrational states, and that a specific rovibrational level of the T_3 state is likely to play a key role in this coupling. They noted that the energy minimum of the seam of intersection between S_1 and T_3 had been predicted to occur in the energy vicinity of $\tilde{A}^1 A_u$ $3\nu_3$ (Refs. 4–6) and at a geometry close to that of the near-linear turning point of the S_1 $3\nu_3$ level. They also pointed out that T_3 does not possess sufficient vibrational state density at the energy of $\tilde{A}^1 A_u$ $3\nu_3$ to account for the observed degree of fractionation, and thus hypothesized that the role of T_3 is to mediate the coupling of the $\tilde{A}^1 A_u$ $3\nu_3$ level to the bath of $T_{1,2}$ states—the *doorway-mediated* coupling hypothesis.

In 1994, Drabbels *et al.*⁷ recorded a high resolution (18 MHz) LIF spectrum of the $V_0^3 K_0^1$ and $V_0^4 K_0^1$ subbands. They observed a background dark-state density on the order of $10/\text{cm}^{-1}$, which was approximately consistent with the expected density of T_1 states in this energy region. A later work⁸ reconsidered this density of states calculation and showed the properly symmetry-sorted $T_1 + T_2$ state density to be in good agreement with the observed value. On the assumption of a direct singlet-triplet coupling model, Drabbels *et al.* used the Lawrance-Knight deconvolution algorithm⁹ to extract the zeroth-order energies of the dark states and their coupling strengths to the bright S_1 state.

In addition to laser-induced fluorescence-based measurements, another class of experiments has exploited the magnetic properties of the dark triplet states not directly accessible by zero-field techniques. Dupré *et al.*¹⁰ reported ZAC experiments, exciting the $\nu_3=0-3$ levels of the $\tilde{A}^1 A_u$ state. In a ZAC measurement, a single S_1 rovibrational level is excited and the intensity of the resulting fluorescence is monitored, while the strength of an external magnetic field is scanned (typically over a range of 0–8 T). States containing triplet electronic state character and therefore possessing a magnetic dipole moment are tuned in energy; when such a

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state is tuned into degeneracy with the fluorescing bright state, it mixes appreciable dark-state character into the bright state, resulting in a decrement to the fluorescence signal (due mainly to enhanced collisional quenching of the longer-lived eigenstate). The resulting anticrossing spectrum gives a panoramic view of the nearby (within up to ~ 7.5 cm $^{-1}$ for a maximum field strength of 8 T) triplet spin-rovibronic states capable of being Zeeman-tuned into resonance with the optically populated S_1 level. These acetylene ZAC spectra also showed a dramatic increase in the number of anticrossings with increasing excitation of the $\tilde{A}^1 A_u \nu_3$ mode; but with the possible exception of a single very broad anticrossing, which will be reconsidered later in this paper, none of the observed anticrossings could be assigned to triplet states of definite vibrational and rotational (K_a, N) quantum numbers.

Finally, a third type of experiment, surface electron ejection by laser excited metastables (SEELEM),¹¹ has been performed. This technique offers direct sensitivity to both triplet and singlet fractional basis state characters. SEELEM spectra of the $V_0^3 K_0^1$ band, recorded simultaneously with UV-LIF spectra,¹² revealed a dense manifold of predominantly triplet-character eigenstates. Subsequently, various statistical measures were devised¹³ to characterize the intensity contours of the SEELEM lines. These statistical measures confirmed a doorway mediated as opposed to a direct mechanism of intersystem crossing.

II. ASSIGNED $T_3 \sim S_1$ PERTURBATIONS

Reference 8 contains the most exhaustive analysis yet attempted of a simultaneously recorded UV-LIF and SEELEM data set in the region of the $V_0^3 K_0^1$ band (around 45 300 cm $^{-1}$). The UV-LIF data set displayed a very large ($\sim 10^4$) dynamic range of intensity, and numerous assignments of singlet and triplet perturbers of $S_1 3\nu_3$ were made. One of the key results of that work is the identification of a rotational series of triplet levels that, as a function of J , tune through a $\Delta J=0$, $\Delta K_a=0$ energy resonance with rotational levels of $3\nu_3$. This “local perturbation” was fitted using an effective Hamiltonian model, based on the well-known^{14,15} rotational quantum number dependence of spin-orbit matrix elements in a Hund’s case- b basis. The rotation-independent matrix element extracted from this deperturbation was found to be 0.126 cm $^{-1}$.

It should be noted that a key observation reported in Ref. 8 must be reinterpreted in light of recent experimental results.¹⁶ Specifically, the lines in Table II assigned to the O branch of the $T_3 \leftarrow S_0$ transition have been shown to terminate on states of insufficiently long lifetimes to be triplets; moreover, the temperature dependence of their intensities is suggestive of a singlet-singlet hot band. This in turn casts doubt on the validity of the $T_3 \leftarrow S_0$ Q branch rotational assignments, which should be carefully subjected to similar measurements. In any event, on account of the difficulties in obtaining unambiguous assignments of the highly congested Q branch, these transitions were not included in the present implementation of the deperturbation fit model of Ref. 8, and

so the result for the spin-orbit perturbation matrix element, obtained from the reliably assigned R - and P -branch transitions, remains unaffected.

In addition to this local perturbation between the T_3 doorway state and low- J values of $S_1 3\nu_3$ ($K=1$), probably the strongest isolated singlet-triplet interaction observed to date in acetylene is a very broad Zeeman anticrossing in fluorescence from the rotationless ($J=K=0$) level of the same S_1 vibrational state ($3\nu_3$).^{1,17} From the reported ZAC spectrum,¹⁸ the position of this anticrossing is observed to be at 7.14 T, with a width of 0.66 T. The corresponding energy shift is calculated from the magnetic field strength using the Zeeman relation¹⁷

$$\Delta E = M_S g \mu_B \Delta B, \quad (1)$$

where M_S is the electron-spin space-fixed projection quantum number (± 1 for a pure triplet, assuming the limit of Paschen-Back decoupling), g is the effective g factor (assumed to equal the approximate “bare-electron” value of 2), and $\mu_B = 9.274 \times 10^{-24}$ J T $^{-1}$ is the Bohr magneton. Thus we find a zero-field S_1 , T_3 energy difference for this anticrossing of $|\Delta E| = 6.67$ cm $^{-1}$. The energy of $3\nu_3$ $J=K=0$ is 45 285.7 cm $^{-1}$, thus the zeroth-order energy of the triplet perturber must lie at either 45 279.0 or 45 292.4 cm $^{-1}$. In the presence of the magnetic field, the $J=0$ singlet can mix with a triplet of either $J=1$ or 0, implying $N=2, 1$, or 0, and therefore *a priori* K for the triplet could assume any of the values 2, 1, or 0.

The strength of the singlet-triplet interaction is reflected in the width of the anticrossing; in the classic analysis of Wieder and Eck,¹⁹ it is shown that an isolated anticrossing in the “strong coupling” limit (singlet-triplet coupling element much larger than mean depopulation rates) has a Lorentzian line shape with a full width half maximum given by

$$\Gamma = \frac{1 + \gamma_S/\gamma_T}{(\gamma_S/\gamma_T)^{1/2}} \frac{2V_{ST}}{M_S g \mu_B}, \quad (2)$$

where γ_S and γ_T are the total (radiative plus collisional) depopulation rates of the singlet and triplet states, respectively. Under the simplifying approximation $\gamma_S \approx \gamma_T$, the prefactor reduces to 2, and the singlet-triplet coupling element is given by one-fourth of the anticrossing width, converted to units of energy. Thus the measured width of 0.66 T gives an interaction strength of 0.17 cm $^{-1}$. This measured coupling matrix element can be related to the corresponding zero-field matrix element by the equation²⁰

$$V_{ST}(M_{N_S}) = V_{ST}^{B=0}(e\nu_S, K_S, N_S; e\nu_T, K_T, N_T) \sqrt{2N_S + 1} \times \begin{pmatrix} N_S & 1 & N_T \\ -M_{N_S} & M_{S_T} & M_{N_T} \end{pmatrix}, \quad (3)$$

where $N_S = M_{N_S} = 0$, so that $N_T = 1$ is fixed by the triangle rule. Evaluating the Wigner coefficient with $M_{S_T} = -M_{N_T} = \pm 1$, we find that

$$|V_{ST}^{B=0}| = \sqrt{3} |V_{ST}| = 0.29 \text{ cm}^{-1}. \quad (4)$$

Evaluating the formulas given in Table 1 of Ref. 15, under the assumption that $K_T=0$, we find that the rotational factor

in the zero-field matrix element is equal to unity, and so the non-rotating-molecule matrix element is in fact 0.29 cm^{-1} (under the assumption of $K_T=1$, the result would have to be multiplied by a factor of 2).

This is roughly similar in magnitude to the coupling matrix element between $S_1\ 3\nu_3$ and the $K=1$ component of the T_3 perturber, extracted from the UV-LIF spectrum. This suggests that these $K=0$ and $1\ S_1\ 3\nu_3 \sim T_3$ interactions are two local perturbations by the $K_a=0$ and 1 rotational submanifolds of the same T_3 vibrational state. The smaller possible value of the zeroth-order energy falls approximately 21 cm^{-1} below the energy of $S_1\ 3\nu_3$; thus it is plausible to assign the anticrossing triplet perturber as the $K=0$ component of the same T_3 vibrational level that appears in our UV-LIF spectrum, provided that we can show this to be a reasonable $K=0$, $K=1$ energy separation for a vibrational level of the T_3 state.

The relationship between the measured two-level $T_3 \sim S_1$ interaction matrix element and the derived nonrotating molecule vibrational matrix element could be distorted by unknown factors, such as dilution of $S_1\ 3\nu_3$ and T_3 perturber characters into the quasicontinuum of T_2 , T_1 , and S_0 vibrational levels, the diabaticization of the $T_3 \sim T_2$ interaction, and the $S_1\ 3\nu_3 \sim 2\nu_3$ ($2\nu_{\text{Bend}}$) [$\nu_{\text{Bend}} = \nu_4 + \nu_6$] anharmonic plus a -type Coriolis interactions currently under analysis. Any estimate of the uncertainties of the derived matrix element would be imprudent.

The decisive factor with respect to the likelihood of additional $T_3 \sim S_1$ vibrational near degeneracies is the magnitude of the A -rotational constant, which governs the coarse rotational spacings between subbands associated with different values of K , the magnitude of the projection of rotational angular momentum along the a (least moment of inertia) axis. It would be helpful to have a grasp of the dependence of this quantity on the T_3 vibrational quantum numbers, in order to gauge the rotational spacings of the T_3 excited vibrational levels. In particular, we expect that A_ν will be altered in a complicated manner by excitation of the symmetric CCH bending and torsional modes (as well as by a -type Coriolis interactions).

III. VIBRATIONAL ASSIGNMENT

A. New *ab initio* determination of the diabatic T_3 minimum

Both the ZAC measurement, on the one hand, and the deperturbation model used to interpret the UV-LIF/SEELEM data set, on the other, provide estimates of spin-orbit matrix elements between S_1 and T_3 perturbors. To an excellent approximation, this matrix element factors into the product of a purely electronic matrix element of the spin-orbit operator and a vibrational overlap integral. The latter can be estimated if something is known about the equilibrium structures and the force fields near the equilibrium geometry of the respective electronic states. The equilibrium geometry and force field can be computed by *ab initio* methods. Precisely such a calculation has already been carried out for T_3 acetylene by Cui and Morokuma,⁶ who computed H^{SO} between S_1 and T_3 at several nuclear configurations. At the minimum of the

seam of intersection in C_2 symmetry between the S_1 and T_3 surfaces, this matrix element (i.e., $\langle \Psi(S=0, M_S=0) | H^{SO} | \Psi(S=1, M_S=1) \rangle$) is 13.7 cm^{-1} . This in turn implies a vibrational overlap integral for the T_3 perturber of $0.126/13.7=0.01$.

This raises two questions: Can we compute a vibrational overlap of this magnitude with $S_1\ 3\nu_3$ for *any* low-lying vibrational level of T_3 ? Do the overlaps computed for the lowest-lying levels show any *diagnostic trends* with vibrational quantum numbers that might aid in proposing or at least narrowing down the vibrational assignment possibilities for the T_3 perturber? To answer these questions, we must examine the complicated T_3 potential energy surface in more detail.

Ab initio electronic structure calculations have been slow in arriving at a consensus regarding the location and nature of the minimum of the T_3 potential energy surface. Cui and Morokuma⁶ were only able to locate a transition state (saddle point), with one imaginary normal mode frequency along an antisymmetric CCH bending coordinate. More recently, Ventura *et al.*²¹ performed extended multireference electron correlation calculations on all four of the lowest-lying acetylene triplet potential energy surfaces. These authors were able to find a genuine minimum (no imaginary frequencies) belonging to the T_3 surface and described its equilibrium structure, although they provided no normal mode vibrational frequencies or eigenvectors. Ventura *et al.* describe two seams of $T_2 \sim T_3$ conical intersections that lie very close to the predicted T_3 stationary point. This complicated topography accounts for the difficulties encountered in locating stationary points.

In order to shed light on the nature of the T_3 potential energy surface, with a view of producing an accurate estimate of this crucial vibrational overlap integral, we have carried out new *ab initio* calculations. To treat the interactions between T_2 and T_3 , we employ a simple diabatic model in which the T_3 and T_2 electronic states are coupled by the two nontotally symmetric modes, ν_5 (antisymmetric CCH stretch) and ν_6 (antisymmetric CCH bend). To estimate the adiabatic couplings, we write the diabatic electronic Hamiltonian matrix \mathbf{U} in the basis spanned by ϕ_1 and ϕ_2 , which are the diabatic wave functions associated with T_3 and T_2 , respectively. Within the harmonic approximation, the diabatic potential energy curves U_{11} and U_{22} expressed in the dimensionless normal coordinates $q=(\omega/\hbar)^{1/2}Q$ are given by

$$U_{11} = \langle \phi_1 | \mathbf{U} | \phi_1 \rangle = \frac{1}{2} \omega_5 q_5^2 + \frac{1}{2} \omega_6 q_6^2, \quad (5)$$

$$U_{22} = \langle \phi_2 | \mathbf{U} | \phi_2 \rangle = \frac{1}{2} \omega_5 q_5^2 + \frac{1}{2} \omega_6 q_6^2 + \Delta, \quad (6)$$

where Δ is the vertical excitation energy between the T_3 and T_2 states at the reference C_2 saddle point on the T_3 surface. In Eqs. (5) and (6) we have assumed that modes ν_5 and ν_6 have the same frequencies (ω_5 and ω_6 , respectively) in the T_3 and T_2 diabatic states.^{22,23} Since the two states are diabatic, they are coupled by the adiabatic vibronic coupling operator U_{12} which can be expanded in a Taylor series in q_5 and q_6 .^{24–26}

TABLE I. Computed structures at the diabatic T_3 minimum.

	pVDZ	pVTZ	pVQZ	Ventura <i>et al.</i> ^a
r_{CC} (Å)	1.381	1.349	1.347	1.352
R_{CH} (Å)	1.101	1.075	1.077	1.079
θ_{CCH} (°)	132.6	137.4	137.3	138.7
τ_{HCCH} (°)	104.7	104.6	104.5	106.1

^aReference 21.

$$U_{12} = U_{21} = \langle \phi_1 | \mathbf{U} | \phi_2 \rangle = \lambda_5 q_5 + \lambda_6 q_6 + \lambda_5' q_5^3 + \lambda_6' q_6^3 + \dots$$

$$\approx \lambda_5 q_5 + \lambda_6 q_6, \quad (7)$$

where we retain only the linear terms in q_5 and q_6 in Eq. (7).

To make contact with properties obtained from quantum chemistry codes, we must switch to the adiabatic representation. The two-dimensional adiabatic potential surfaces $E^+(q_5; q_6)$ and $E^-(q_5; q_6)$ are obtained by diagonalization of the diabatic electronic Hamiltonian matrix

$$\begin{pmatrix} U_{11} & U_{12} \\ U_{21} & U_{22} \end{pmatrix} = \begin{pmatrix} (1/2)\omega_5 q_5^2 + (1/2)\omega_6 q_6^2 & \lambda_5 q_5 + \lambda_6 q_6 \\ \lambda_5 q_5 + \lambda_6 q_6 & (1/2)\omega_5 q_5^2 + (1/2)\omega_6 q_6^2 + \Delta \end{pmatrix}. \quad (8)$$

The two roots of this Hamiltonian, which represent the adiabatic energy curves, are

$$E^\pm(q_5, q_6) = \frac{1}{2}(\omega_5 q_5^2 + \omega_6 q_6^2 + \Delta) \pm \frac{\Delta}{2} \left[1 + \frac{4(\lambda_5 q_5 + \lambda_6 q_6)^2}{\Delta^2} \right]^{1/2}, \quad (9)$$

where E^+ and E^- are the adiabatic potential energy surfaces of the T_2 and T_3 states, respectively. Therefore, the second derivative of each of these roots yields the adiabatic harmonic frequencies Ω_5^\pm and Ω_6^\pm

$$\Omega_5^\pm = \left[\frac{\partial^2 E^\pm(q_5, q_6)}{\partial q_5^2} \right]_{q_5=q_6=0} = \omega_5 \pm \frac{2\lambda_5^2}{\Delta}, \quad (10)$$

$$\Omega_6^\pm = \left[\frac{\partial^2 E^\pm(q_5, q_6)}{\partial q_6^2} \right]_{q_5=q_6=0} = \omega_6 \pm \frac{2\lambda_6^2}{\Delta}. \quad (11)$$

Using Eqs. (10) and (11), the diabatic frequencies ω_5 and ω_6 are given by

$$\omega_5 = \frac{\Omega_5^+ + \Omega_5^-}{2}, \quad (12)$$

$$\omega_6 = \frac{\Omega_6^+ + \Omega_6^-}{2}, \quad (13)$$

and the adiabatic vibronic coupling coefficients are then given by

TABLE II. *Ab initio* adiabatic coupling parameters.

	pVDZ	pVTZ	pVQZ
Δ (eV)	0.0461	0.0296	0.0281
$ \lambda_5 $ (eV)	0.0308	0.0226	0.0220
$ \lambda_6 $ (eV)	1.101	1.075	1.024
ω_5 (cm ⁻¹)	2965.0	3041.7	3036.5
ω_6 (cm ⁻¹)	474.6	370.4	397.6

$$|\lambda_5| = \frac{[\Delta(\Omega_5^+ - \Omega_5^-)]^{1/2}}{2}, \quad (14)$$

$$|\lambda_6| = \frac{[\Delta(\Omega_6^+ - \Omega_6^-)]^{1/2}}{2}. \quad (15)$$

To utilize this diabatic model one must calculate, using quantum chemistry methods, the following adiabatic quantities: Δ , Ω_5^\pm , and Ω_6^\pm . We employed the equation of motion coupled cluster with singles and doubles (EOM-CCSD) method for all geometry optimizations and harmonic frequency calculations. The correlation-consistent basis sets of Kendall *et al.*²⁷ denoted by cc-pVXZ, where X stands for D (double), T (triple), or Q (quadruple) zeta quality, were used. All EOM-CCSD calculations were performed using the ACES II set of programs²⁸ with analytic gradients for both geometry and harmonic frequency calculations.

The geometries for the C_2 saddle point on the T_3 surface are collected in Table I, with previous results from the literature for comparison. A general decrease in bond lengths and increase in bond angles is observed with larger basis set size. However, when the basis set increases from cc-pVTZ to cc-pVQZ, the difference in geometry is relatively small within the EOM-CCSD approach. The pVQZ results of Table I agree well with the MR-AQCC (TQ)-extrapolated values from Ventura *et al.*²¹

B. Harmonic overlap integrals

The computed parameters for the adiabatic vibronic couplings between T_3 and T_2 were obtained using Eqs. (14) and (15) and are listed in Table II. The diabatic frequencies of T_3 , ω_5 , and ω_6 (rescaled to conventional mass-weighted normal coordinates) are also listed. Within all basis sets, the ν_6 mode, which corresponds to the antisymmetric CCH bend, provides the stronger coupling between T_3 and T_2 .

Now the harmonic frequencies and force constants about the “diabatized” T_3 minimum can be used to compute vibrational overlap integrals with S_1 $3\nu_3$. In order to minimize the error of this calculation, we have also recomputed harmonic frequencies and force constants for S_1 . Tables III and IV list the normal modes and calculated frequencies for S_1 and T_3 , respectively. The calculation also establishes an electronic energy separation ($T_e(S_1) - T_e(T_3)$) of 0.001 2211 hartree = 270 cm⁻¹.

The vibrational overlap integrals are straightforwardly calculated within the harmonic oscillator approximation using the multidimensional generating function formalism developed by Sharp and Rosenstock³¹ and extended by several other authors.^{32,33} The required inputs are the respective nor-

TABLE III. Computed and experimental S_1 vibrational frequencies.

Mode	Predominant character	Calc. (cm ⁻¹)	Expt. (cm ⁻¹) ^a
$\nu_1 (a_g)$	Symmetric CH stretch	3113.8	3004
$\nu_2 (a_g)$	CC stretch	1504.0	1420
$\nu_3 (a_g)$	Symmetric CCH bend	1087.3	1064
$\nu_4 (a_u)$	Out-of-plane torsion	641.5	765
$\nu_5 (b_u)$	Antisymmetric CH stretch	3091.4	2914
$\nu_6 (b_u)$	Antisymmetric CCH bend	732.4	785

^aReferences 29 and 30.

mal mode frequencies and \mathbf{L} matrices, which contain the normal mode eigenvectors expanded in a basis of internal stretch and bend angle coordinates.³⁴

Table V lists the T_3 vibrational states, the harmonic energies of which are predicted to fall within approximately 100 cm⁻¹ of S_1 $3\nu_3$, along with their calculated overlaps with S_1 $3\nu_3$.

C. A-rotational constants

We are now in a position to make some quantitative predictions concerning the vibrationally averaged (diabatic) A-rotational constants discussed earlier. A straightforward calculation determines A_e (the value of A corresponding to our computed equilibrium geometry) as 19.95 cm⁻¹, considerably larger than the value observed for vibrational levels of S_1 (typically ~14–15 cm⁻¹). As is the case for S_1 , the a -inertial axis is tilted away from the C–C bond axis by a slight angle (~6°). The increase in A_0 for T_3 is explained largely by the significantly wider (i.e., less bent) CCH bond angle at the T_3 minimum, which brings the structure closer to linearity and consequently reduces the a -axis moment of inertia. In order to estimate the vibrational dependence of the A-rotational constant for T_3 , we make use of the results of a second-order perturbative treatment, by which one can calculate the vibration-rotation interaction constants α , defined by the power series

$$A_\nu = A_e - \sum_r \alpha_r^A (\nu_r + 1/2) + \dots \quad (16)$$

The result for α_r^A in the harmonic limit is³⁵

$$-\alpha_r^A = \frac{2A_0^2}{\omega_r} \left[\sum_{\xi} \frac{3(a_r^{\xi})^2}{4I_{\xi\xi}} + \sum_{s \neq r} (\zeta_{r,s}^{\alpha})^2 \frac{(3\omega_r^2 + \omega_s^2)}{\omega_r^2 - \omega_s^2} \right], \quad (17)$$

where

TABLE IV. Computed diabatic T_3 vibrational frequencies.

Mode	Predominant character	Calc. (cm ⁻¹)
$\nu_1 (a)$	Symmetric CH stretch	3225.88
$\nu_2 (a)$	Torsion	1626.90
$\nu_3 (a)$	CC stretch	1411.96
$\nu_4 (a)$	Symmetric CCH bend	653.04
$\nu_5 (b)$	Antisymmetric CH stretch	3036.48
$\nu_6 (b)$	Antisymmetric CCH bend	397.56

$$a_r^{\alpha\beta} = \left(\frac{\partial I_{\alpha\beta}}{\partial Q_r} \right)_e = \sum_{\gamma, \delta, \varepsilon} 2\epsilon_{\alpha\gamma\varepsilon} \epsilon_{\beta\delta\varepsilon} \sum_i m_i^{1/2} r_i \gamma_{i\delta, r}, \quad (18)$$

and the constants denoted $\zeta_{r,s}^{\alpha}$ are the Coriolis coefficients that define the components of vibrational angular momentum in terms of the normal coordinates and their conjugate momenta,

$$\pi^{\alpha} = \sum_{r,s} \zeta_{r,s}^{\alpha} Q_r P_s. \quad (19)$$

They are listed in Table VI can be calculated directly from the \mathbf{I} -matrix components as follows:

$$\zeta_{r,s}^{\alpha} = \sum_{\beta, \gamma, i} \epsilon_{\alpha\beta\gamma} J_{\beta i, r} J_{\gamma i, s}. \quad (20)$$

In Eq. (17) above, the first term represents contributions in first-order perturbation theory from the quadratic dependence of the μ tensor, and therefore also of the rotational constant operator, on the normal coordinates. The second term represents the second-order contributions of Coriolis interactions diagonal in J , but which exchange two quanta of nonidentical normal modes. Both classes of terms contribute to the energy a term proportional to $(\nu + 1/2)K^2$, and therefore, a term to the rotational constant linear in $(\nu + 1/2)$.

Carrying out the calculation using the parameters derived from our *ab initio* normal mode analysis for T_3 acetylene, we find α coefficients as given in Table VII. We thus see that the most pronounced effects on A_ν are observed in levels involving the ν_4 symmetric bending and ν_6 antisymmetric bending modes: excitation of ν_4 results in a dramatic *decrease* in A (due primarily to inertia-tensor dependence), while excitation of ν_6 dramatically *increases* A (due predominantly to Coriolis interactions). Zero-point vibrations result in a value of $A_0 = 18.91$ cm⁻¹. Finally, it should of course be noted that for a given vibrational level, the observed same- J $K=0$, $K=1$ energy separation will in fact be $A_{\text{eff}} = A_\nu - (B_\nu + C_\nu)/2 \approx A_\nu - 1$ cm⁻¹.

Examining Table V, we find three T_3 vibrational states lying between 38 and 111 cm⁻¹ from S_1 $3\nu_3$ with an appropriate vibrational overlap (~0.01) with the observed triplet perturber. Of all the computed quantities, we expect the energy to be the least accurate, owing both to error in the frequencies and to neglected anharmonicity. The overlap in-

TABLE V. T_3 vibrational levels predicted to lie in the vicinity of S_1 $3\nu_3$. Five of the overlap integrals are rigorously zero by symmetry.

Vibrational level	$E - E(3\nu_3)$ (cm ⁻¹)	$\langle \psi S_1 3\nu_3 \rangle$	A_ν (cm ⁻¹)
$\nu_2 + 2\nu_4 + \nu_6$	-108	0	24.62
$\nu_3 + 3\nu_4$	-68	0.12	28.82
$\nu_3 + 5\nu_6$	-39	0	11.25
$4\nu_4 + 2\nu_6$	-32	-0.062	26.86
$\nu_5 + \nu_6$	-5	-0.0037	19.19
$\nu_4 + 7\nu_6$	-3	0	9.29
$\nu_2 + \nu_3 + \nu_6$	-3	0	20.05
$\nu_2 + \nu_4 + 3\nu_6$	+34	0	18.09
$2\nu_3 + \nu_4$	+38	0.015	24.25
$\nu_3 + 2\nu_4 + 2\nu_6$	+74	0.011	22.29
$3\nu_4 + 4\nu_6$	+110	0.017	20.33

TABLE VI. Numerical a -axis Coriolis coefficients for T_3 , calculated from an *ab initio* normal mode analysis.

	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6
ν_1	0					
ν_2	0	0				
ν_3	0	0	0			
ν_4	0	0	0	0		
ν_5	0.0093	0.3776	-0.2387	0.0241	0	
ν_6	0.0288	-0.7470	0.4913	-0.0166	0	0

tegrals, by contrast, are expected to be much less sensitive to uncertainty in the computed frequencies. It is seen that the state $2\nu_3 + \nu_4$, with a reasonable A_ν value of 24.45 cm^{-1} , is predicted to lie only 38.0 cm^{-1} higher in energy than $S_1 3\nu_3$. A still higher-energy state at 110.4 cm^{-1} from $3\nu_3$, $3\nu_4 + 4\nu_6$, is predicted to possess an A_ν value closest to that required for the observed simultaneous perturbation of $S_1 3\nu_3$ $K=0$ and $K=1$. We thus tentatively propose these two vibrational levels as leading candidates for the assignment of the twice-sampled (in $K=0$ and 1) T_3 perturber.

IV. ADDITIONAL $T_3 \sim S_1$ NEAR DEGENERACIES

The calculation described in this work establishes a theoretical value for the energy of the T_3 zero-point vibrational level of $41\,860 \text{ cm}^{-1}$. There are therefore, in this approximately 3500 cm^{-1} -wide energy region below $S_1 3\nu_3$, many T_3 vibrational levels capable of interacting, perhaps strongly, with $3\nu_3$ or with another S_1 vibrational level. Indeed, Table V lists one T_3 level, $\nu_3 + 3\nu_4$, which, although lying roughly 100 cm^{-1} in energy from our preferred candidate for the T_3 perturber, is predicted to interact with it an order of magnitude more strongly. Thus this level could experience enough mixing with S_1 to be appreciably illuminated. Careful examination of this region by UV-LIF/SEELEM spectroscopy would be worthwhile. Within an energy region $\pm 300 \text{ cm}^{-1}$ near each S_1 vibrational level, there is likely to be a T_3 vibrational level with vibrational overlap ≈ 0.1 , hence spin-orbit matrix element $\approx 1 \text{ cm}^{-1}$.

V. CONCLUSION

We have undertaken a new *ab initio* characterization of the acetylene T_3 potential energy surface in the vicinity of its stationary point. After accounting for the adiabatic interactions with the T_2 surface, harmonic frequencies and force constants about the diabatic T_3 minimum have been obtained, which enable the calculation of harmonic vibrational overlap integrals with the $3\nu_3$ vibrational level of S_1 for the entire manifold of low-lying T_3 vibrational states. On the basis of these quantities, a small number of T_3 states that lie in the energetic region of $S_1 3\nu_3$ has been found to possess overlaps of the correct magnitude for the triplet perturber of

this level. Two of these, the $2\nu_3 + 3\nu_4$ and $3\nu_4 + 4\nu_6$ levels, are predicted to possess a coarse rotational structure consistent with the observed perturbations of $S_1 3\nu_3$ at both $K=0$ and 1, unifying UV-LIF/SEELEM measurements with a much earlier Zeeman anticrossing observation. Experiments are in progress to locate additional T_3 levels with the goal of adding a few more experimental calibrations of the T_3 diabatic potential energy surface and $S_1 \sim T_3$ and $T_3 \sim T_{1,2}$ spin-orbit coupling strengths.

ACKNOWLEDGMENT

This work has been supported by the Air Force Office of Scientific Research (Grant No. AFOSR-FA9550-05-1-0077).

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TABLE VII. Calculated a -axis vibration-rotation interaction coefficients for T_3 .

	α_1	α_2	α_3	α_4	α_5	α_6
Eq. (17)	-0.25	-0.71	-0.40	-2.49	-0.25	+2.03

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